



COMMENTS OF INVENTOR

Amano et al. teach an apparatus comprising an annular catalyst bed defined by the space between an inner and an outer cylindrical surface, wherein the annular catalyst bed comprises spiral plates to effect a spiral flow of gases through the catalyst bed. The inventors claim the intended use of the apparatus is for the reaction between natural gas and steam (reforming reaction) for the production of hydrogen-enriched gas (reformate). The inventors claim that the object of the invention is to miniaturize the reforming apparatus by enhancing the conductivity and reactivity and to prevent the (physical) destruction of the catalyst by partially supporting the weight of the catalyst on the spiral plates.

The reforming reaction referenced by the inventors is endothermic and requires the supply of heat to the catalyst bed. In conventional practice, the reforming reaction is conducted over a nickel-containing catalyst operating at high temperature typically in the range of 1000°F to 1550°F. These catalysts are specifically formulated to accommodate operation at high temperature without loss of catalytic activity due to thermal sintering.

Amano et al. does not teach the use of helical flow guides for exothermic reactions that require the removal of heat. Amano et al. also does not teach the use of helical flow guides for critical control of catalyst bed temperature, such as needed for application to catalytic reactions using highly temperature-sensitive catalysts that are prone to thermal sintering and subsequent loss of catalytic activity.

Amano et al. teach an apparatus to supply endothermic heat of reforming reaction by heat transfer from a high temperature heat source (such as combustion products) to an outer cylindrical surface that is in communication with an inner annular catalyst bed comprising spiral plates that enhance heat conductivity and reactivity to miniaturize the apparatus.

Amano et al. does not teach the use of helical flow guides to remove exothermic heat by heat transfer from an outer annular catalyst bed through an inner cylindrical surface that is in communication with a steam generator.

The invention of this action (Application No. 09/709,616) describes an apparatus to maximize hydrogen production by exothermic reaction between carbon monoxide and steam, such as found in reformat. The invention

teaches the use of helical flow guide surfaces to enhance removal of heat from an outer annular catalyst bed to an inner cylindrical surface that is in communication with a steam generator. The specific object of the invention is to maintain a critical balance between exothermic heat generated by the kinetic reaction and heat removal accomplished by virtue of design in order to maintain a range of temperatures within the catalytic bed that are both kinetically and thermodynamically favorable for reaction yield while protecting the catalyst from deactivation due to thermal sintering. The invention of Amano et al. does not teach the optimization of product yield and the protection of thermally-sensitive catalyst by virtue of a helical flow guide design.

The exothermic reaction between carbon monoxide and steam is commonly known as the Water-Gas Shift (WGS) reaction. The WGS reaction is used to maximize the yield of hydrogen contained in reformat produced by the reforming reaction between natural gas and steam. In typical industrial practice, the WGS reaction of reformat feed is conducted in two sequential adiabatic stages, each operating within distinct temperature ranges, wherein heat is removed between the stages. The first stage, known in the art as the High Temperature Shift (HTS) reactor, operates in the

temperature range of 550°F to 800°F using catalyst containing mixtures of iron and chromium. The second stage, known in the art as the Low Temperature Shift (LTS) reactor, operates in the temperature range of about 380°F to 500°F using catalyst containing mixtures of copper and zinc.

The LTS reactor is beneficial because the WGS reaction is thermodynamically favored at lower temperature. However, the LTS catalyst is temperature-sensitive and exhibits a loss of catalytic activity due to thermal sintering if exposed to temperatures above about 500°F for prolonged periods. Because the WGS reaction is exothermic, reformat can not be processed using a single adiabatic LTS reactor since the accompanying temperature rise over the catalyst, as a result of equilibrium reaction, would damage the catalyst. If an LTS reaction could be designed to directly process reformat using a single-stage, non-adiabatic reactor while maintaining temperatures in the optimum kinetic and thermodynamic regime and simultaneously avoiding catalyst deactivation, it would provide significant economic benefit for future hydrogen generation applications.

The invention disclosure of this action addresses this object by stating:

"The use of a low temperature reactor is beneficial because the water-gas shift reaction is thermodynamically favored at lower temperature. However, a high temperature shift reactor is generally required to limit the amount of heat that is released in the low temperature shift reactor.

Conventional low temperature shift catalysts comprise a mixture of copper and zinc that are supported on a ceramic carrier. These catalysts promote the water-gas shift reaction at lower temperature, but lose activity if they are exposed to excessively high temperatures due to sintering of active metals. Therefore, it is generally desirable to limit the maximum temperature of the low temperature shift catalyst to about 500°F in order to achieve long catalyst life.

The water-gas shift reaction releases approximately 9837 calories per gram-mole of carbon monoxide that is consumed. If the water-gas shift reaction were conducted using a single adiabatic low temperature shift

reactor, the heat release would result in a temperature increase across the catalyst bed that would exceed the desirable temperature limit for conventional low temperature shift reactors. Furthermore, the high exit temperature from the water-gas shift reactor would be thermodynamically less favorable for achieving high conversions of carbon monoxide.

There is a need to minimize the number of reactors and heat exchangers that are needed to achieve the objective of high conversion of carbon monoxide for PEM fuel cell applications, in order to reduce the size, cost and complexity of the fuel processor. Therefore, it is desirable to conduct the water-gas shift reaction using a single reactor vessel that is maintained within acceptable operating temperature limits by controlling heat removal from the reactor.

The steam reforming reaction requires large quantities of steam for the conversion of hydrocarbon to reformat. It is desirable to recover the heat released from the water-gas shift reaction for the purpose of

*generating steam in order to improve the thermal efficiency of the fuel processor. The present invention achieves the objective of temperature control and heat recovery by integrating a lower temperature shift reactor within a steam generator that contains water boiling at a temperature range of about 360°F to 400°F, corresponding to a boiler pressure of about 153 psia to 247 psia."*

The invention disclosure of this action describes a single-stage, non-adiabatic LTS reactor apparatus using a catalytic bed with helical flow guide surfaces for optimum transfer of exothermic heat from an outer annular space containing a LTS catalyst to an inner cylindrical heat transfer surface that is in communication with a steam generator. The invention disclosure provides specific criteria for boiler temperature, catalyst space velocity, and catalyst annulus dimension to achieve optimum reactor yield and catalyst life.

For instance, when exothermic heat is transferred from an outer annular catalyst bed to an inner heat transfer surface, a temperature gradient will exist within the catalyst bed between the outer wall of the annular catalyst bed and the inner wall of the annular catalyst bed that is

in contact with inner the heat transfer surface. If the temperature gradient is too large, the outer wall of the annular catalyst bed can overheat. By maintaining a high gas velocity in the annular space by virtue of the helical flow guide surfaces and by limiting the thickness of the annular catalyst bed dimensions as specified in the invention disclosure, the temperature gradients in the annular catalyst bed can be minimized. Furthermore, since the helical flow guide surfaces are connected to both the inner and outer walls of the annular catalyst bed and are in direct thermal communication with other intermediate regions of the catalyst bed, the helical flow guide surfaces act as extended heat transfer surfaces to further reduce the temperature gradients within the annular catalyst bed. There are no teachings in the prior art as cited by the Examiner for the use of helical flow guide surfaces within an annular catalyst bed for the object of protecting temperature-sensitive catalysts, such as Cu/Zn catalysts used to conduct exothermic reactions, such as the WGS reaction. The prior art also does not teach the use of controlled annular catalyst dimensions and the benefits of helical flow guide surfaces that act as an extended heat transfer surface to limit temperature gradients in temperature-sensitive catalysts.



To further clarify, Collins et al. discloses the use of a multiplicity of tubular LTS reactors that are vertically disposed within an annular steam generator. Specifically Collins describes *"Each low temperature shift reactor 414 comprises a tube 436 which is filled with a suitable low temperature shift reaction catalyst 438, for example copper/zinc low temperature shift catalyst. The low temperature shift reactors 414 pass axially, with respect to the vessel 418, through the steam generator."* Collins does not suggest the use of a single outer annular catalyst bed that surrounds an inner cylindrical steam generator, such as disclosed in this invention application.

The use of a multiplicity of tubular LTS reactors vertically disposed in a steam generator, as suggested by Collins, provides a means to achieve a high ratio between the available heat transfer surface and the LTS catalyst volume. Therefore, the invention of Collins did not consider the problems associated with temperature gradients within the exothermic and temperature-sensitive LTS catalyst beds. However, the use of a multiplicity of LTS reactors is less economic than the use of a single LTS reactor, particularly for relatively small-scale applications.

The invention disclosure of this application describes a cost-effective solution using a single annular LTS reactor that surrounds an inner cylindrical steam generator. Because of the use of a single annular LTS catalyst bed, special attention is given to the control of temperature within the LTS bed to achieve optimum conversion and long catalyst life. Temperatures are controlled within the single annular LTS catalyst bed by employing helical flow guide surfaces that increase the turbulence and heat transfer from the LTS catalyst bed to the inner cylindrical steam generator walls. The helical flow guide surfaces also act as heat transfer fins to enhance the rate of heat transfer from all regions of the annular catalyst bed, but particularly from the outer zones of the annular catalyst bed, to the inner cylindrical steam generator walls. The invention disclosure of this application achieves the object of simplicity and economy and also achieves the object of optimum product yield and protection of temperature-sensitive catalyst activity.

The invention disclosure of this action provides detailed experimental data to support the achievement of this object. The combined features of this invention are not obvious to a person having ordinary skill in the art. Significant commercial investment has been made by world renown companies over the last several decades to develop

economically beneficial hydrogen generation technology, such as encompassed by the current invention disclosure. If the subject invention were obvious to a person of ordinary skill in the art, the concept would have been proven in commercial use.

The Examiner cites the current invention as being unpatentable over Collins et al. in view of Amano et al. We believe the Examiner does not recognize the novel aspects of the invention with regard to the combination of design economy and technical features that afford unique temperature control of an exothermic LTS reaction using catalyst susceptible to thermal deactivation.

In summary, the current invention is not obvious with respect to the combined patents of Collins and Amano for the following reasons:

1. The invention of Amano teaches the use of spiral plates for application to endothermic reforming reactions, typically using nickel-containing catalyst, that are operated at high temperature in the range of 1000°F to 1550°F. The object of the Amano invention is to enhance conductivity and reactivity in order to miniaturize the

reformer tube and to physically support the catalyst to prevent its physical destruction (e.g. by crushing). The Amano invention is heated from the outside by heat transfer from high temperature combustion products. The Amano invention does not suggest its use for low temperature or exothermic reactions or combinations thereof. The Amano invention does not teach the removal of exothermic from an outer annular catalyst bed to an inner cylindrical steam generator. The Amano invention does not teach the protection of temperature-sensitive catalysts using helical flow guide surfaces. The Amano invention does not teach the use of helical flow guide surfaces as extended heat transfer surfaces.

2. The Amano invention relates to reactions, catalysts, process conditions, and objects that are far removed from the invention of this action.

3. The invention of Collins et al. teaches use of a multiplicity of LTS reactors vertically disposed in an annular steam generator. The Collins invention does not suggest the use of a single annular LTS reactor concentrically disposed around an inner cylindrical steam generator also containing waste heat transfer conduits. The invention of Collins does not suggest the use of helical

flow guide surfaces for critical temperature control of exothermic, temperature-sensitive reactions.

4. The Collins invention relates to LTS reactions contained in a multiplicity of LTS reactors disposed in a steam generator. The Collins inventions does not address the needs of a single annular LTS reactor concentrically disposed around an inner cylindrical steam generator.